

PB85-116127

Removal of Heavy Metals by
Artificial Wetlands

San Diego Region Water Reclamation Agency
Santee, CA

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

Oct 84



U.S. Department of Commerce
National Technical Information Service

NTIS

EPA-600/D-84-258
October 1984

THE REMOVAL OF HEAVY METALS BY ARTIFICIAL WETLANDS

by

Richard H. Gersberg and Stephen R. Lyon
Ecological Research Associates
San Diego, CA 92116

Bert V. Elkins
San Diego Region Water Reclamation Agency
Santee, CA 92071

Charles R. Goldman
University of California
Davis, CA 95616

Cooperative Agreement CR807299

EPA Project Officer
Lowell E. Leach

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ADA, OK 74820

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO. EPA-600/D-84-258	2.	3. RECIPIENT'S ACCESSION NO. PB8 5 116127
4. TITLE AND SUBTITLE The Removal of Heavy Metals by Artificial Wetlands	5. REPORT DATE October 1984	
7. AUTHOR(S) Richard M. Gersberg, Stephen R. Lyon, Bert V. Elkins, and Charles R. Goldman	6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS San Diego Region Water Reclamation Agency 10887 Woodside Avenue Santee, CA 92071	8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS R. S. Kerr Environmental Research Laboratory U. S. Environmental Protection Agency P. O. Box 1198 Ada, OK 74820	10. PROGRAM ELEMENT NO. B113	11. ~~EXTRACURRICULAR~~ Coop. Agr. CR807299
15. SUPPLEMENTARY NOTES	13. TYPE OF REPORT AND PERIOD COVERED Final 3/17/82 - 3/16/83	
16. ABSTRACT Artificial wetlands have been operated successfully for treatment of municipal wastewater for a number of years at several locations in this country. However, the capability of these systems to treat heavy metal laden municipal wastewater had not previously been investigated. The artificial wetland system at Santee, California which is normally used for polishing secondary municipal wastewater was evaluated for treatment of cadmium, zinc and copper. These metals were added to the influent waste stream in high concentrations during a one-year study and wetland effluent was tested to determine their removal efficiency. Their removal efficiency ranged from an average of 97 percent for zinc to over 99 percent for the two other metals.	14. SPONSORING AGENCY CODE	
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS Sewage treatment Chemical Removal Water pollution Industrial waste	b. IDENTIFIERS/OPEN ENDED TERMS Land application Aquaculture Artificial wetlands Heavy metal removal	c. COSATI Field/Group 43F 68D
18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 12
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

THE REMOVAL OF HEAVY METALS BY ARTIFICIAL WETLANDS

Richard M. Gersberg
Director of Research

Stephen R. Lyon
Chief Chemist
Ecological Research Associates
4674 Arizona Street
San Diego, California 92116

Bert V. Elkins
Project Manager
San Diego Region Water Reclamation Agency
10887 Woodside Avenue
Santee, California 92071

Charles R. Goldman
Professor, University of California
Davis, California 95616

INTRODUCTION

Heavy metals are ubiquitous environmental pollutants which arise from a variety of industrial, commercial, and domestic activities. New pretreatment standards promulgated by the United States Environmental Protection Agency require many industrial dischargers, such as electroplating and metal finishing operations, to limit heavy metal levels to very low residual concentrations (1); however, many other industries, including foundries, electronics, mining, smelting, pulp and paper, tanning, photo processing, and fertilizer and chemical manufacturing can also be a significant source of heavy metals to the environment. Furthermore, studies show that heavy metals can be found in municipal sewage treatment plants receiving little or no industrial discharge (2). Considering the toxic nature of heavy metals, and the fact that conventional treatment processes at municipal sewage plants are for the most part inadequate for complete dissolved metal removal (3), it is obvious that a real need exists for low-cost tertiary treatment processes to accomplish this task.

There are a number of technologies available for the removal of heavy metals from wastewater, including chemical precipitation, electrolysis, reverse osmosis, and ion exchange. However, for the most part, these methods involve high capital and O&M expense or generate large amounts of bulky sludges with long settling times (4). The concept of using wetlands for cost-effective and energy-efficient treatment of municipal or industrial wastewaters has been demonstrated both in Europe (5,6) and in the United States (7-9) with a high degree of success. Indeed, both saltwater and freshwater wetlands, have been shown to remove trace metals through precipitation - adsorption reactions in the sediments as well as uptake by the marsh plant community (10,11). Such integrated treatment has been shown to have considerable economic and operational advantages over individual systems designed specifically for a single task, such as metal removal

by chemical precipitation (12).

This report will describe studies in Santee, California using artificial wetlands which offer an integrated approach to meeting treatment aims of metal removal by combining biological, as well as physico-chemical treatment in a simple, low-energy process. Such artificial wetlands may replace natural wetlands in the many treatment situations where the natural ecosystems are geographically unavailable at a treatment site or environmentally endangered by human perturbations.

METHODS AND MATERIALS

The artificial wetlands consisted of plastic-lined (Hypalon, 30 mil) excavations containing emergent vegetation growing in gravel. The marsh beds were trapezoidal trenches, 18.5 m long x 3.5 m wide x 0.76 m deep. The secondary effluent from the existing activated sludge treatment plant (Santee Water Reclamation Facility of Padre Dam Municipal Water District, Santee, California) was used as the influent to the wetland beds. A 10-channel peristaltic pump was used to enrich the surface inflow to individual wetland beds with either cadmium (Cd) as $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, copper (Cu) as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, or zinc (Zn) as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. In the case of the Cu and Zn amended beds, the inflow was also acidified (with H_2SO_4) to pH 5.5 to keep the metals from precipitating on addition, and also to test the capability of the wetlands to shift the pH of an acid waste stream towards neutrality.

Dissolved copper was analyzed by the bathocuproine technique from Standard Methods (13). Dissolved zinc and cadmium were analyzed by potentiometric stripping analysis (PSA). In PSA, the analytes are pre-concentrated in a mercury film (plated) by potentiostatic reduction and amalgamation. The potentiostat is then disconnected and the reduced analytes are oxidized by a suitable oxidizing agent. A redox titration curve is thus obtained and registered on a high impedance recorder. The accuracy of PSA has been tested against anodic stripping voltametry and atomic absorption spectrometry and has been shown to compare well. The precision was less than 0.1 ppb for cadmium, zinc, and copper. The detection limit is in the order of 0.5 ppb and the analytical range is 0.1 - 1000 ppb (14).

Oxygen was measured using a YSI 54A Oxygen meter. Oxidation-reduction potential was determined using an Orion 407A Ion Analyzer with redox probe, and pH was measured using an Ecolab 102 B meter.

Effluent samples were collected by pumping water from a standpipe reaching to the bottom at the effluent end of each bed. Influent samples were collected at a point downstream of where the metal stock solution was mixed with the wastewater just before the flow entered the surface of the wetlands. Samples were preserved with acid and refrigerated until analysis. Valves at the inflow and outflow end of each bed were used to regulate the hydraulic application rate and control the water level. The beds were kept flooded throughout the period of study.

RESULTS AND DISCUSSION

Figure 1 shows the pilot-scale artificial wetland beds, four of which received secondary municipal wastewater effluent amended with the toxic heavy metals Cu, Zn, and Cd. Figure 2 shows the levels of dissolved Cu in the inflow and the outflow of two wetlands beds (one planted in *Scirpus sp.* and one in *Typha sp.*) enriched with Cu for the period from November, 1982 through July, 1984. Wetlands bed 5W was initially enriched to a mean inflow Cu level of 2.22 mg l^{-1} , this subsequently increased to a mean inflow concentration of 9.26 mg l^{-1} from March, 1983 through June, 1984. During this latter period, at the hydraulic application rate of 8 cm per day, the mean effluent Cu level from bed 5W was 0.056 mg l^{-1} , for a Cu removal efficiency of 99%. Wetland bed 3W, its inflow at the lower hydraulic application rate of 4.7 cm per day, showed virtually the same treatment efficiency (99%), with the mean inflow Cu level of 10.68 mg l^{-1} reduced to an effluent level of 0.059 mg l^{-1} during the period from February, 1983 through June, 1984. The fact that the Cu removal efficiencies at both of the hydraulic application rates tested were 99%, underscores the possibility that these wetlands could sustain such efficient treatment at even higher application rates, thus reducing the capital expense by reducing the wetland area required for treatment of a given volume of wastewater.

Figure 3 shows the level of Zn and Cd in the inflow and outflow of two wetland beds (both planted in *Scirpus sp.*) which were enriched with Zn and Cd for the period from June, 1983 through September, 1983 and September, 1983 through July, 1984, respectively. The mean Zn removal efficiency was 97%, with the mean inflow (application rate = 4.7 cm per day) of 11.28 mg l^{-1} reduced to 0.37 mg l^{-1} in the wetland effluent. Similarly, wetland treatment reduced the mean inflow (application rate = 4.7 cm per day) Cd concentration of 0.532 mg l^{-1} to less than 0.004 mg l^{-1} in the effluent (for a mean Cd removal efficiency of 99%).

Only in the Zn-amended bed was there any significant trend of increasing effluent metal level as a function of length of operation (with highest values in spring of 1984), but the Zn removal efficiency still never fell below 88%. The data presented above demonstrate the high capacity of these artificial wetlands for the removal of dissolved heavy metals over long-term operation.

Dissolved metal entering a wetland ecosystem may be removed from the water by precipitation (as insoluble metal salts) and sedimentation, adsorption onto inorganic and organic solids, and incorporation into living biomass. The wetlands can therefore be viewed as an integrated reactor, which removes heavy metals through a combination of physical, chemical and biological processes.

A quantitative assessment of the amount of metal removed by plant uptake can be made based upon plant productivity measurements and values for typical concentrations of Cu and Zn in aquatic plant biomass. In plants grown in metal contaminated environments, levels of Cu and Zn range from 10-150 ppm (10,15,16). Using a value of 12 g dry wt per m^2 per day for the mean productivity of the vegetation of the artificial wetlands (17) then it can be calculated that plant uptake may account for only 120 - 1800 μg Cu per m^2 or less than 1% of the total amount of Cu or Zn in the inflow to beds 3W or 4W (approximately 500 mg per m^2 per day).

At such high wastewater application rates, the predominant mechanisms of removal of both copper and zinc in the artificial wetlands are likely due to precipitation or adsorption reactions. Although there was little evidence of any significant accumulation of metal-laden sludge at the bottom of the wetlands, in the Cu-amended bed, a blue precipitate was found to cover the surficial gravel substrate and also coat the decomposing ground litter. An important fact to consider here, is that the metabolism by the biotic components of the wetland ecosystem can raise the pH of the inflowing acidic waters to values near neutrality. Our results show that in both the Cu and Zn amended beds, the influent pH of about 5.6 was increased to a mean value of 6.9 at the effluent end. Moreover, in the standing surface waters during an algal bloom, the pH reaches values in the range of 8.5 - 9.5 during the day as a result of algal photosynthesis. Under these circumstances, precipitation of metals is more favored, as the responsible precipitating anions (S^{2-} , CO_3^{2-} , PO_4^{3-} , OH^{-1}) increase as a fraction of the total soluble species (18).

In other anaerobic environments of the wetlands, mostly within the gravel substrate, bacterial sulfate reduction generates sulfides. Due to their high reactivity with metal ions, and their insolubility over a broad pH range, these sulfides can play an important role in metal precipitation. Studies in both freshwater and saltwater wetlands have shown that anoxic sediments can act as large sinks for heavy metals (10,11). The importance of adsorbed forms of metals in wetlands has also been discussed, but remains largely unassessed (15,19). Dead litter are known to adsorb metals, and both fulvic and humic acids released by litter decomposition is known to form complexes with metals (15). To date, methodology for the quantitative assessment of precipitation-adsorption phenomena are only for single metal species in defined media (18), and it is likely that they would have little relevance in describing the complex interactions occurring within a wetland ecosystem. Nevertheless, our results point to the fact that these artificial wetlands behave in a similar manner to natural wetlands, where precipitation and adsorption in anoxic sediments contribute to the predominant fraction of overall metal removal observed.

Previous investigations using artificial wetlands as wastewater treatment systems have been reported (5,8,20), but none have focused upon monitoring the efficiency of heavy metal removal. Our studies show that at the wastewater application rate of 4.7 cm per day, approximately 1 acre of wetlands would be required to treat 50,000 gpd of wastewater flow. The capital cost for this area of constructed wetlands would be about \$0.83 per 1000 gallons treated (amortized at 15% over a 10-year period). For comparison, the capital cost of a chemical precipitation plant is in the order of \$2.24 per 1000 gallons (4).

The process design of these artificial wetlands is simple and they require no chemical addition. The only significant O&M cost is a periodic harvest of the biomass (once or twice per year). Continued monitoring over an extended period will allow us to estimate the length of time these wetlands may be used before the accumulated metal-laden sediments interfere with proper operation and must be suitably disposed of. Overall, these artificial wetlands appear to be an attractive alternative for small to medium sized industries or municipalities which are attempting to meet their treatment needs of

metal removal, while being receptive to a low-cost and environmentally sound, emerging technology.

SUMMARY

1. Artificial wetlands receiving secondary municipal wastewater were enriched with the heavy metals Cu, Zn, and Cd. At the hydraulic application rate of 4.7 cm per day (residence time equal to about 5.5 days), removal efficiencies were 99%, 97%, and 99%, respectively. As the higher hydraulic application rate of 8 cm per day, the Cu removal efficiency remained at 99%.
2. The predominant removal mechanisms in the artificial wetlands were attributed to precipitation-adsorption phenomena. Precipitation was enhanced by wetland metabolism which increased the pH of inflowing acidic waters to near neutrality.
3. At the hydraulic application rate of 4.7 cm per day, approximately one acre of constructed wetlands would be required to treat 50,000 gallons per day of wastewater flow.
4. The capital cost for these artificial wetlands is lower than alternative processes such as chemical precipitation.

ACKNOWLEDGEMENTS

The authors would like to thank D. Allen, L. Heydon, I. Cotton, and C. Loss for technical support, and the staff of the Santee Water Reclamation Facility of Padre Dam Municipal Water District (E. Houser, Manager), Santee, California for providing space and facilities. The California Department of Water Resources (Grant B-53459), the U.S. Environmental Protection Agency (Grant CR 807299-03-3), and the San Diego Region Water Reclamation Agency provided financial support.

DISCLAIMER

The information in this article has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement CR807299 to the San Diego Region Water Reclamation Agency. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

1. Federal Register. "Electroplating and Metal Finishing Point Source Categories; Effluent Limitations, Pretreatment Standards, New Source Performance Standards." Fed. Regist. 48, 137 (1983).
2. Klein, L.A., et al., "Sources of Metals in New York City Wastewater." J. Water Pollut. Control Fed. 46, 2653 (1974).
3. Oliver, B.G. and Cosgrove, E.G., "The Efficiency of Heavy Metal Removal by a Conventional Activated Sludge Treatment Plant." Water Res. 8, 869 (1974).

4. McIntyre, G. et al., "Inexpensive Heavy Metal Removal by Foam Flotation." J. Water Pollut. Control Fed. 55, 1144 (1983).
5. Seidel, K., "Macrophytes and Water purification." In "Biological Control of Water Pollution." J. Tourbier, and R.W. Pierson (Eds.), University of Pennsylvania Press, Philadelphia, Pa. 109 (1976).
6. deJong, J., "The Purification of Wastewater With the Aid of Rush or Reed Ponds." In "Biological Control of Water Pollution." J. Tourbier, and R.W. Pierson (Eds.), University of Pennsylvania Press, Philadelphia, Pa., 161 (1976).
7. Small, M., "Marsh/Pond Sewage Treatment Plants." In "Freshwater Wetlands and Sewage Effluent Disposal." D.L. Tilton, et al. (Eds.), The University of Michigan, Ann Arbor, Mich., 197 (1976).
8. Spangler, F.L., et al., "Experimental Use of Emergent Vegetation for the Biological Treatment of Municipal Wastewater in Wisconsin." In "Biological Control of Water Pollution." J. Tourbier, and R.W. Pierson (Eds.), University of Pennsylvania Press, Philadelphia, Pa., 161 (1976).
9. Gersberg, R.M., et al., "Wastewater Treatment by Artificial Wetlands." Water Sci. Tech. In Press.
10. Banus, M.D., et al., "Lead, Zinc and Cadmium Budgets in Experimentally Enriched Salt Marsh Ecosystems." Estuar. Coastal Mar. Sci. 3, 421 (1975).
11. Lindau, C.W. and Hossner, L.R., "Sediment Fractionation of Cu, Ni, Zn, Cr, Mn, Fe in One Experimental and Three Natural Marshes." J. Environ. Qual. 11, 540 (1982).
12. Smith, R. and Wiechers, S.G., "Elimination of Toxic Metals from Wastewater by an Integrated Wastewater Treatment/Water Reclamation System." Water SA 7, 65 (1980).
13. American Public Health Association., "Standard Methods for the Examination of Water and Wastewater." 15th Edition. APHA, Washington, D.C. (1980).
14. Jagner, D. and Kirstin, A., "Derivative Potentiometric Stripping Analysis with a Thin Film of Mercury on a Glassy Carbon Electrode." Anal. Chim Acta 100, 375 (1978).
15. California State Water Resources Control Board, "The Environmental Requirements of Aquatic Plants." In "The Use and Potential of Aquatic Species for Wastewater Treatment." Publication No. 65, California-SWRCB, Sacramento, California (1980).
16. Gallagher, J.L. and Kibby, H.V., "Marsh Plants as Vectors in Trace Metal Transport in Oregon Tidal Marshes." Amer. J. Bot. 67, 1069 (1980).

17. Gersberg, R.M. et al., "Nitrogen Removal in Artificial Wetlands." Water Res. 17, 1009 (1983).
18. Callander, I.J. and Barford, J.P., "Precipitation, Chelation, and the Availability of Metals as Nutrients in Anaerobic Digestion. I. Methodology." Biotechnol. and Bioeng. 25, 1947 (1983).
19. Miller, R.W., "The Role of Humic Acids in the Uptake and Release of Mercury by Freshwater Sediments." Verh. Internat. Verein. Limnol. 19, 2082 (1975).
20. Gersberg, R.M. et al., "The Use of Artificial Wetlands to Remove Nitrogen from Wastewater." J. Water Pollut. Control Fed. 56, 152 (1984).

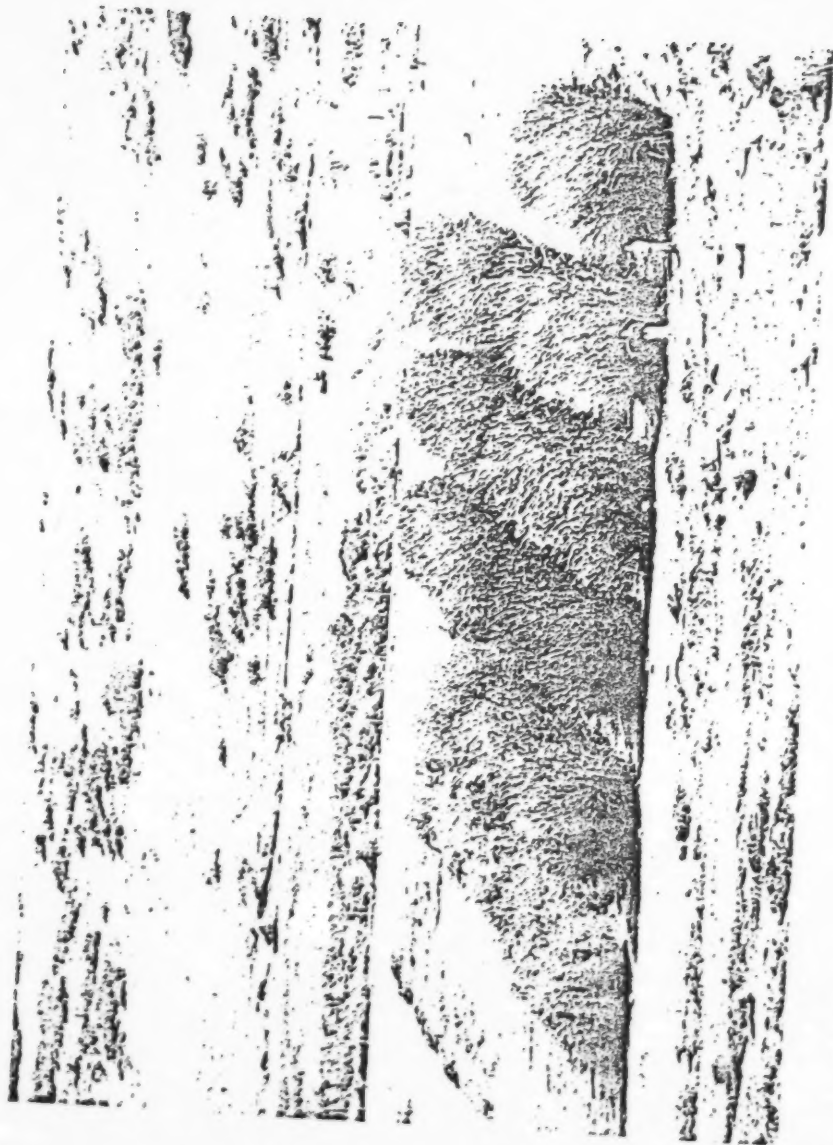


Figure 1. Photograph of artificial wetlands site at the Santee Water Reclamation Facility. For scale, note the two persons standing at right in foreground. Each of the twelve marsh beds are 18.5m long x 3.5m wide x 0.70m deep. The vegetation ranges from 3 to 4m in height.

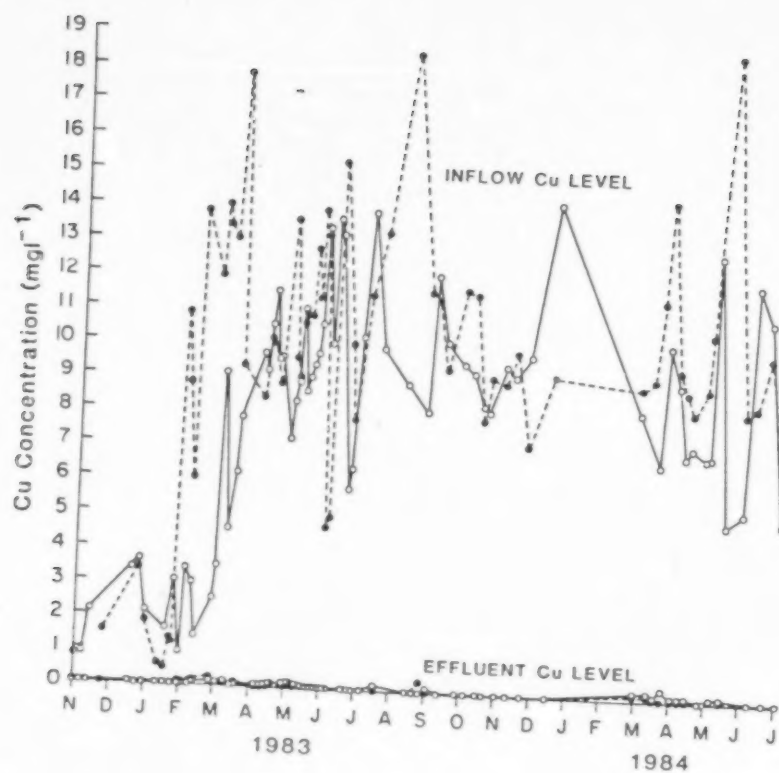


Figure 2. The levels of dissolved Cu in the inflow and the outflow of wetland bed 5W (○), planted in *Typha* sp., and wetland bed 3W (●), planted in *Scirpus* sp. Hydraulic application rates were 8 cm per day (residence time = 3.2 days) for 5W and 4.7 cm per day (residence time = 5.5 days) for 3W.

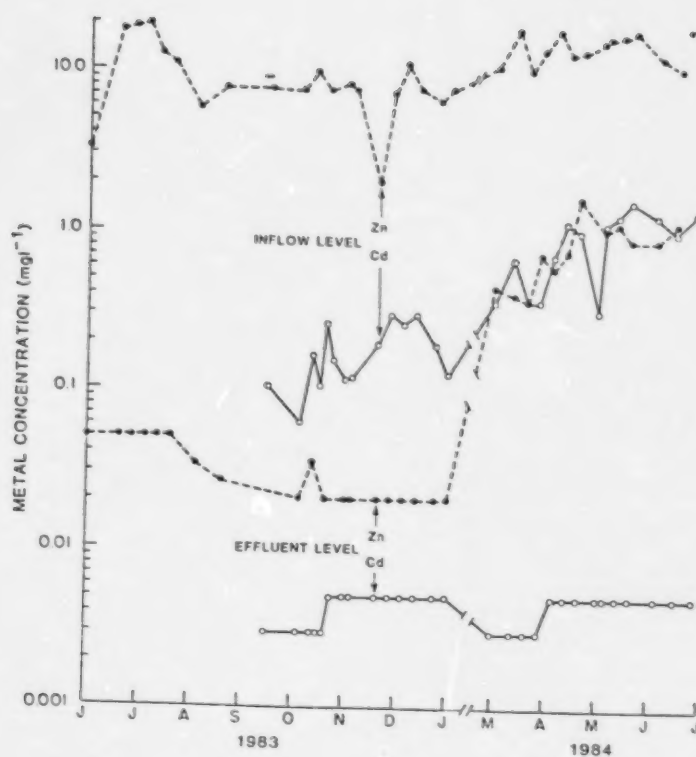


Figure 3. Semi-log plot of the levels of Zn and Cd in the inflow and outflow of two wetland beds (both planted in *Scirpus* sp.). The hydraulic application rate was 4.7 cm per day (residence time = 5.5 days) for both plots.